Rotational resonances in molecular scattering of ultra-low-energy electrons*

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A detailed study is made of the nature of rotational Feshbach resonances in the elastic scattering of extremely-low-energy electrons by diatomic polar molecules. The bound-state properties of an electron in the field of a dipole rotator, determined previously, are used in establishing the resonance behavior of elastic-scattering phase shifts in the energy region below the first rotational excitation threshold. Feshbach resonances of very narrow widths are found in partial-wave scattering channels with total angular momenta greater than zero when the strength of the interaction potentials is somewhat less than that necessary to yield bound states of the same symmetry type, and very much less than those necessary to yield a "bound state" of the projected Hamiltonian QHQ. The latter implies a non-negligible value of the resonance energy shift for polar molecules.

I. INTRODUCTION

The existence of rotational resonances in low-energy electron collisions with simple molecules has been proposed[1] to explain anomalies in electron swarm experiments at very high pressures[2-7] and in electron-beam transmission experiments with time-of-flight techniques.[8] In these experiments the energy regime is well below thresholds for electronic or vibrational excitation of the target system. The existence of temporary negative ions, or resonances, associated with electronically and vibrationally excited states of molecular systems is well known, but no theoretical demonstration has yet been made of such states associated with rotational excitation. Close-coupling results for e-H_2 scattering failed to show any theoretical evidence for such phenomena,[9] though experiments[8] seem to indicate their presence.

In order to explore the nature of possible rotational resonances in molecular scattering phenomena, particularly for polar molecules, we have considered the problem of electron scattering by a simple dipolar system in the energy region below the first rotational excitation threshold. Any resonances in this energy region must of necessity be either Feshbach-type[10] rotational resonances associated with virtual excitation of the target system to a rotationally excited state, or simple shape resonances associated with the penetration of a potential barrier in one or more angular-momentum components of the elastic-scattering channels.

The existence of Feshbach-type rotational resonances in electron scattering by a simple dipole rotator is essentially guaranteed for proper choices of moment of inertia, dipole strength, and electron energy. The relevant binding properties of such target systems in various rotational states have already been well established.[11] Thus this provides an ideal system for the present study.

This point has been demonstrated recently by Bottcher[12] in a model study of electron scattering by a rotating dipole in which he analyzed a simple two-state approximation to scattering by a dipolar system with a hard-sphere repulsive core.

II. METHOD

It has been well established that thermal energy momentum transfer and elastic cross sections for electrons on polar molecules cannot be determined to any reasonable degree of approximation by considering only the dipole contribution to the electron-molecule interaction potential.[13] However, rotational excitation cross sections show a very strong correlation with the square of the dipole moment of the target system and are reasonably well represented by the result obtained from the Born approximation. (For highly polar molecules, where the Born approximation becomes inadequate, this correlation is destroyed and the rotational excitation cross section is inadequately determined by the dipole field alone, as is true in general for the other cases mentioned above.[13]) Thus for the purpose of investigating resonances associated with rotational excitation of polar molecules, the dipole field is of primary importance in determining the nature of such phenomena, though for the case of a real molecule the other contributions to the interaction potential would strongly shift the position of any such resonances on a scale of dipole strengths and/or incident energy.

We consider a simple dipolar molecular system which is composed of point charges of opposite sign, $\pm q$, separated by distance R with moment of inertia I and rotational energy levels $E_j = j(j+1)/2I$. (The separation distance has been chosen as $R = 2s = 0.667a_0$.[11]) The system has dipole moment $D = qR$ and is capable of binding an electron to form a negative ion in a state of total angular momentum

J only if the dipole moment exceeds a critical value D_J^c as described in an earlier paper.[11]

We write the total time-independent Schrödinger equation for the problem as

$$H\Psi(\vec{r}, \hat{s}) \equiv [T + H_{rot} + V(\vec{r}, \hat{s})]\Psi(\vec{r}, \hat{s}) = E\Psi(\vec{r}, \hat{s}).$$

(1)

Here T is the kinetic-energy operator for the projectile, H_{rot} is the rotational Hamiltonian of the target system, and V is the projectile-target interaction potential.

The total wave function Ψ_{jl}^{JM} for the electron-target system having total angular momentum J can be written as[14]

$$\Psi_{jl}^{JM}(\vec{r}, \hat{s}) = \sum_{j'l'} Y_{j'l'}^{JM}(\hat{r}, \hat{s}) \frac{U_{j'l'}^{J}(r)}{r},$$

(2)

where $Y_{j'l'}^{JM}(\hat{r}, \hat{s})$ is the usual coupled spherical harmonic which is an eigenfunction of the rotational Hamiltonian and of J^2. The vector $\vec{r}$ designates the electron coordinate and $\hat{s}$ is the orientation vector of the molecular axis. The use of (2) in Eq. (1) leads to the set of radial equations[14]

$$\left(-\frac{d^2}{dr^2} + \frac{l'(l'+1)}{r^2} - k_{jj'}^2\right) U_{j'l'}^{J}(r)$$

$$+ \sum_{j''} \sum_{l''} \sum_{\mu} f_{\mu}(j''l'', j'l'; J) V_{\mu}(r) U_{j''l''}^{J}(r) = 0.$$

(3)

$U_{j'l'}^{J}(r)$ is the reduced radial function of the scattered electron whose orbital angular momentum at large distance is l'. The momentum l' couples to the rotational angular momentum j' of the target to give total angular momentum J. The coefficients $f_{\mu}(j'', l''; j'l', J)$ result from angular integration over the functions Y_{jl}^{JM} and over the angular part of the multipole component $V_{\mu}(r)$ of the interaction potential.[11, 14] We use rydberg atomic units where the unit of length is a_0, the Bohr radius, and the unit of energy is the rydberg, 13.6 eV. Thus $k_{jj'} = [E_j - j'(j'+1)/2I]^{1/2}$, where E_j is the total energy of the system when the target is in rotational state j. $E_j = E_{incident} + j(j+1)/2I$.

In order to discuss resonance structure in the scattering cross sections which result from solutions of Eq. (3) it is convenient, following Feshbach,[10] to write the coupled equations (3) formally as

$$P(H_{rot} + T + V - E)P\Psi = -PHQ\Psi,$$

(4a)

$$Q(H_{rot} + T + V - E)Q\Psi = -QHP\Psi,$$

(4b)

where the projection operator P projects onto the open-channel subspace and Q projects onto the closed-channel subspace of the total space spanned by the eigenfunctions of H. These operators satis-

fy the familiar relations $P + Q = 1$; $P^2 = P$; $Q^2 = Q$; $PQ = 0$. If Eq. (4b) is solved formally for $Q\Psi$ and the result substituted into (4a) the equation becomes

$$P\left(H_{rot} + T + V - PHQ\frac{1}{Q(H-E)Q}QHP - E\right)P\Psi = 0.$$

(5)

The term $PHQ[Q(H-E)Q]^{-1}QHP$ is the optical-potential operator of Feshbach and the remaining terms make up the close-coupling operator, which is obtained by retaining only the *open* channels in the expansion of Eq. (2). Since we are interested in scattering phenomena below the first excitation threshold, the optical-potential terms contain all contributions from rotationally excited states of the target system. For polar molecules these contributions are very large. Resonance properties of Eq. (5) are most easily described by following the usual practice of expanding the optical-potential term through use of the eigenfunctions of QHQ. Thus we define the eigenfunction Φ_n by

$$QHQ\Phi_n(\vec{r}, \hat{s}) = \epsilon_n \Phi_n(\vec{r}, \hat{s}).$$

(6)

By using the representation Φ_n for the optical potential, Eq. (5) becomes

$$P\left(H - \sum_n \frac{PHQ|\Phi_n\rangle\langle\Phi_n|QHP}{\epsilon_n - E} - E\right)P\Psi = 0.$$

(7)

In the neighborhood of an eigenvalue, say, ϵ_i, of QHQ, i.e., $E \approx \epsilon_i$, the ith term in (7) becomes large. If this term is explicitly separated out of Eq. (7) we have

$$P(H' - E)P\Psi = -\frac{PHQ|\Phi_i\rangle\langle\Phi_i|QHP\Psi}{E - \epsilon_i},$$

(8)

where

$$H' = PHP + \sum_{n \neq i} \frac{PHQ|\Phi_n\rangle\langle\Phi_n|QHP}{E - \epsilon_n}.$$

Equation (8) can be solved formally to give

$$P\Psi = P\Psi_0 + \frac{1}{E - \epsilon_i} GPH\Phi_i\rangle\langle\Phi_i QHP\Psi\rangle,$$

(9)

where G is the Green's function of the operator $H' - E$. If Eq. (9) is multiplied through by $\langle\Phi_i QHP$ and the resulting expression for $\langle\Phi_i QHP\rangle$ is substituted back into (9) these manipulations yield

$$P\Psi = P\Psi_0 + \frac{GPHQ\Phi_i\rangle\langle\Phi_i QHP\Psi_0\rangle}{E - \epsilon_i - \Delta_i},$$

(10)

where

$$\Delta_i = \langle\Phi_i QHPGPHQ\Phi_i\rangle$$

(11)

is the shift in the resonance energy caused by the interaction of the closed with the open channels.

The resonance position is at an energy $E = \epsilon_i + \Delta_i$. The "width" can be shown to be

$$\Gamma_i = 2\pi |\langle \Psi_0 PHQ\Phi_i \rangle|^2 \tag{12}$$

and the resonance part of the phase shift is given by

$$\tan\eta_r = -(\tfrac{1}{2}\Gamma_i)(E - \epsilon_i - \Delta_i)^{-1}. \tag{13}$$

One may determine approximate resonance energies by solving Eq. (6), which corresponds to the elimination of the open channel in the coupled set (3). However, to obtain more complete information about any such resonances, including the energy shifts Δ_i and widths Γ_i of Eqs. (11) and (12), additional effort is required. For polar systems the Green's function is not easily obtained and this approach is consequently very difficult. In addition, we wish to obtain the range of values of the dipole moment of a target system which will lead to resonant structure in a given channel. This information is important for its implications in electron scattering by molecular systems and is not readily available from the results represented by Eq. (10). Thus, in the present study the coupled equations (3) were solved directly to obtain detailed information on scattering resonances. In order to eliminate any ambiguities in the interpretation of these results, the eigenvalue equation (6) for QHQ was also solved for the special cases of zero-energy eigenvalues and zero binding energy in Q space (i.e., $\epsilon = E_1$, where E_1 is the inelastic threshold energy). The relevance of this information will be discussed below.

If we consider solutions to (3) in the energy regime below the first excitation threshold, that is, where $E < 1/I$ Ry, then all rotational excitation channels are closed and only elastic scattering is possible. The appropriate boundary conditions on the coupled set (3) for scattering from ground-state molecules become

$$U^J_{j'l'}(r) \underset{r\to 0}{\sim} \alpha_{jl'} r^{l'+1} \quad \text{for all } j'l', \tag{14a}$$

$$U^J_{j'l'}(r) \underset{r\to\infty}{\sim} 0 \quad \text{for } j' > 0, \tag{14b}$$

$$U^J_{0l'}(r) \underset{r\to\infty}{\sim} \sin(k_0 r + \delta_{l'}) \quad \text{for } j' = 0. \tag{14c}$$

Eigenvalues of QHQ are obtained by eliminating the $j = 0$ component in set (3). The appropriate boundary conditions for this problem are (14a) and (14b).[11]

The coupled equations (3) were solved numerically by starting solutions at the origin through a Froebenius expansion and integrating outward by a Numerov integration procedure. Consideration was given only to scattering below the first inelastic threshold. In this case all but one of the constants α_{jl} were chosen to give exponentially decaying solutions for the closed channels; that is, to

satisfy (14b). The final constant and the elastic phase shift δ_l were then determined from condition (14c). Eigenvalues of QHQ were obtained in a manner analogous to that used in determining critical dipole moments for electron binding.[11] Only the special cases of zero-energy eigenvalues and zero-energy electron binding were solved, where the energy was held fixed and the magnitude of D varied to satisfy (14a) and (14b). The detailed numerical procedures were identical to those described earlier (see Appendix I of Ref. 11).

III. RESULTS

In order to get a detailed picture of the behavior of elastic-scattering phase shifts in the vicinity of a resonance, we first determine the nature of the nonresonant phase shifts as a function of dipole strength. This is the contribution from the H' term in Eq. (8). Thus we show in Fig. 1 the $J = 0$ and $J = 1$ nonresonant partial-wave phase shifts for a *fixed* energy of 1×10^{-6} Ry as a function of dipole moment. The phase shifts increase by π rad as the dipole moment goes through a critical value for the particular choice of J and I. The lowest critical moments for $J = 0$–3 are given in Table I and are indicated in Fig. 1 as D^c_0, D^c_1, etc.

If resonant structure is indeed found in scattering phase shifts, it is sometimes necessary to look further to determine the nature of the phenomenon; for example, whether the observation is that of a
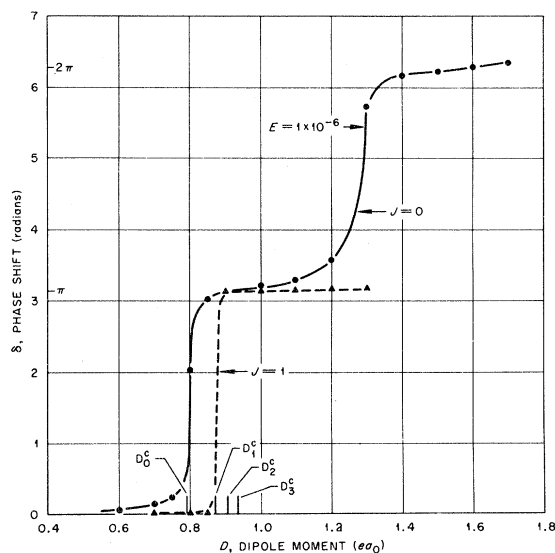

FIG. 1. S- and P-wave phase shifts as a function of dipole moment for a fixed energy, $E = 1 \times 10^{-6}$ Ry. The target system has moment of inertia $I = 1 \times 10^4 ea_0^2$, charge separation $R = 0.667a_0$, and charges $\pm q$ such that $D = qR$.

TABLE I. Critical moments for a rigid dipole rotator of charge separation $R = 0.667a_0$ and moment of inertia $I = 5 \times 10^3 m_e a_0^2$. D is in ea_0 units.

J	D_J^c	$D_{QHQ}^{\epsilon=0}(J)$	$D_{QHQ}^{\epsilon=E_1}(J)$
0	0.796	3.23	3.22
1	0.870	1.06	0.933
2	0.907	0.914	0.902
3	0.935	0.935	0.928

shape resonance or a Feshbach-type resonance associated with a real or virtual transition of the target to an excited state. Since the latter are, by definition, associated with eigenvalues of QHQ, it is useful to know something about this spectrum. It was not feasible to obtain the eigenvalues of QHQ as a function of D. However, it is quite useful to know the minimum dipole moment of the present target system which will give a "bound state" in Q space. Thus the critical dipole moment necessary to yield an eigenvalue $\epsilon = 0$ in Eq. (6) was obtained for $J = 0-3$. These are tabulated in column 3 of Table I as $D_{QHQ}^{\epsilon=0}(J)$. More useful in the present context would be information on the range of dipole moments which yield a lowest eigenvalue ϵ, which is below the first inelastic threshold. This information was obtained by setting $\epsilon = E_1$, where E_1 is the threshold excitation energy, in Eq. (6) and solving for the dipole moment which yields this particular eigenvalue. These are tabulated as $D_{QHQ}^{\epsilon=E_1}(J)$ in column 4 of Table I. For lower values of D the eigenvalues of QHQ cross over into the energy region above the first inelastic threshold.

Note that the J dependence of $D_{QHQ}^{\epsilon}(J)$ is rather different from that of D_J^c. The lowest dipole moment necessary to bind an electron in the $J = 0$ state in Q space is much larger than the corresponding critical moment D_0^c for binding to the ground-state dipole rotator. For $J = 1$ the critical moment $D_{QHQ}^{\epsilon=E_1}(1)$ is only slightly larger than D_1^c and for $J = 2$ the two are almost equal. Note also the interesting fact that the decreasing trend in $D_{QHQ}^{\epsilon}(J)$ reverses with $J = 3$ with the result that the critical value for $J = 2$ is a minimum. This behavior can be understood from an examination of two competing effects in electron binding in Q space. First, there is the effective decrease in the dipole field experienced by the electron as a result of rotation. A rotating field source tends to decrease the average field experienced by a weakly bound electron, causing a tendency for D_{critical} to increase with higher J. This tendency is true for D_J^c and $D_{QHQ}^{\epsilon}(J)$. Second, in the case of critical binding in Q space there is an important effect due to the deletion of the elastic channel. In the limit of zero energy all channels are closed, and it is well

known that each closed channel included in the target eigenstate expansion (2) makes an added contribution to the electron-target interaction potential. In the formation of the eigenvalue equation for QHQ the $j = 0$, $l = J$ orbital is absent from the coupled equations and as a result the effective binding is decreased. Thus in the present context the deletion of the ground-state component of (2) automatically implies that the dipole moment necessary to yield a zero-energy eigenvalue of QHQ will be greater than that necessary to yield the same eigenvalue for the full Hamiltonian. Note however that as J increases the deleted orbital, which has $l = J$, plays a decreasing role in its contribution to the interaction potential.[15] Thus the zero-energy critical moments of QHQ and of H should become indistinguishable for large J. This means that $D_{QHQ}^{\epsilon}(J)$ must eventually increase with J for large J, as exhibited by the results of Table I.

In Fig. 2 sample results are shown for the S-wave phase shift $(J = 0)$ where the electron is scattered from a ground-state target system. Results are plotted for several different dipole moments, both subcritical and supercritical in magnitude. The energy range is from 10^{-6} Ry to the threshold for rotational excitation of the target system ($E = 2.0 \times 10^{-4}$ Ry with the present choice of moment of inertia). The $J = 0$ partial-wave component shows no unusual behavior, as is evident from the figure. For targets whose dipole moments are less than the lowest critical value for the $J = 0$ state the phase shift goes to zero at zero energy. For moments greater than D_0^c the phase converges to π rad at zero energy, as predicted by Levinson's theorem.[16] The results of Fig. 1 indicate that the critical moment for the existence of a second $J = 0$ bound state occurs near $D = 1.30$, where the phase
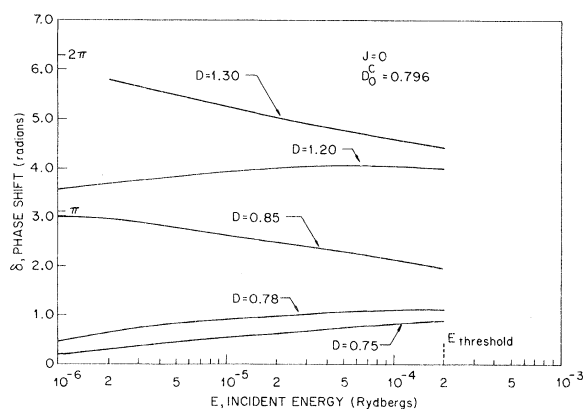

FIG. 2. S-wave phase shift $(J = 0)$ as a function of energy for target systems of dipole moments $D = 0.75$, 0.78, 0.85, 1.20, and $1.30 ea_0$. The critical moment for $J = 0$ is $D_0^c = 0.796 ea_0$ (Ref. 11).

shift tends toward 2π rad at $E = 0$.

The S-wave results shown in Fig. 2 exhibit no resonance behavior and would hardly be worthy of discussion but for a recent study by Bottcher[12] of electron scattering by a rotating dipole. In his analysis Bottcher solved a simple approximate model for dipolar scattering in which the sum over angular-momentum states in Eq. (3) was truncated to include only two terms, and the dipolar field was simulated through the use of a hard-sphere repulsive core to remove the point dipole singularity at the origin. In contrast to the present results for S-wave scattering, his approximate two-state model gave pronounced resonant structure under conditions which are exactly analogous to those of the present study. These were referred to as "shape" resonances,[12] as opposed to normal Feshbach resonances, which are associated with virtual excitation to a closed channel. We should note that there is no centrifugal barrier to be penetrated in the $J = 0$ partial-wave channel. Thus there is no possibility of a shape resonance in the usual definition of the term. We also note that no Feshbach resonance associated with virtual excitation to the $j = 1$ rotational state of the target is possible for dipole moments in the range studied here or in Ref. 12, since the lowest critical moment for such a resonance is of the order of $3.2ea_0$, as shown in Table I.

Finally, there is the possibility of a resonance (or false resonance) in the elastic S-wave channel when the dipole moment of the target system is somewhat less than that necessary to yield a real bound state for the electron-dipole system.[17-19] The results of Ref. 12 seem inconsistent with this process, however, since resonant structure was found for both supercritical and subcritical dipolar systems. We infer that the structure in the S-wave phase shifts in Bottcher's study is dependent on the approximate model which he solved.

Now consider the higher-angular-momentum partial-wave components of the wave function for the electron-dipole system. For each of the $J > 0$ states of the system, an eigenvalue of QHQ exists for dipole moments which are near the critical moment for that rotational state of the system (Table I). These lead to ordinary Feshbach resonances in the energy region below the first rotational excitation threshold.

Sample results for the $J = 1$ elastic channel ($j = 0$, $l = 1$ asymptotically) are shown in Fig. 3 for several different values of D. First consider the results for a dipole rotator having $D = 0.85ea_0$. This is just below the lowest critical value for the $J = 1$ state of the full Hamiltonian but some 20% below the corresponding critical moment of QHQ. A narrow resonance is clearly observed at an energy of
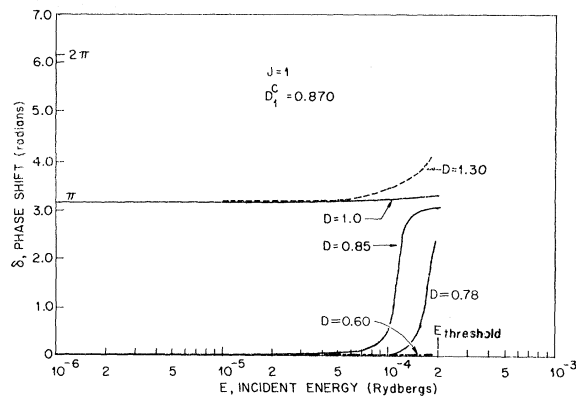

FIG. 3. P-wave phase shift ($J = 1$) as a function of energy for target systems of dipole moments $D = 0.60$, 0.78, 0.85, 1.0, and $1.30ea_0$. The critical moment for $J = 1$ is $D_1^c = 0.870ea_0$ (Ref. 11).

1.1×10^{-4} Ry with a width of $\sim 0.4 \times 10^{-5}$ Ry. In the case of a somewhat smaller dipole moment, $D = 0.78ea_0$, the lowest eigenvalue ϵ_i of QHQ is increased and the resonance occurs at a higher energy, as shown in Fig. 3. For even smaller D the position of the resonance moves further up in energy and finally crosses the lowest inelastic threshold (at $E = 2 \times 10^{-4}$ in our example). Under this condition the elastic and inelastic cross sections will be expected to exhibit broader resonances in the energy region between the first and second inelastic thresholds.[16] In the present example this occurs for $D \sim 0.75ea_0$.

Now if the dipole moment is *increased* in magnitude the eigenvalue ϵ_i decreases, causing the resonance to move to lower energies. At the critical value $D = 0.870$ the resonance moves to $E = 0$ and the phase shift moves up to π rad. This behavior is shown in Fig. 3 for a supercritical case, $D = 1.0ea_0$. Finally, at $D \sim 1.30$, a second eigenvalue of QHQ appears and another resonance is observed in the cross section, as shown in the final curve in Fig. 3.

One characteristic of the resonant P-wave phase shifts shown in Fig. 3 should be further noted. Resonant structure occurs for a dipole field which is considerably weaker than that necessary to sustain an eigenvalue of QHQ in the elastic energy region. Mathematical difficulties did not allow determination of the lowest eigenvalue, ϵ, of QHQ for a given interaction potential, which precluded an exact determination of the resonance energy shift Δ. However, it is obvious from Table I that for $D = 0.85$ the $J = 1$ eigenvalue is greater than E_1. Since the actual resonance energy in this instance is about 0.9×10^{-4} Ry below the threshold energy E_1, the resonance energy shift Δ in Eq. (10) is in excess of 0.9×10^{-4} Ry. This shift is small in ab-
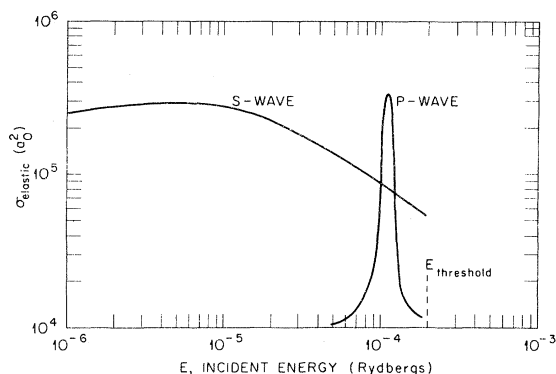
FIG. 4. S- and P-wave contributions to the elastic-scattering cross section in the region below the first rotational excitation threshold. $D = 0.85 ea_0$ and the lowest inelastic threshold occurs at $E = 2 \times 10^{-4}$ Ry.

solute value but it represents a very large percentage change in the resonance energy from that which would be inferred by taking the eigenvalue ϵ_i as a zeroth-order approximation to the actual value.

An example of structure in the elastic section in the region below the first inelastic threshold is shown in Fig. 4. The $J = 0$ and 1 contributions are shown separately. The resonance in the $J = 1$ phase shift leads to a very pronounced peak in the elastic cross section near $E_{\text{threshold}}$.

We thus have the result that, associated with a given critical moment, a rotational Feshbach resonance can occur in a system whose dipole moment lies within a certain range ΔD of the critical value. This range extends from $D = 0.75$ to 0.87 in the $J = 1$ partial wave for the system just described. The Feshbach formalism outlined earlier leads immediately to the conclusion that similar resonances will occur in higher-angular-momentum states of the electron-dipole system. In the present instance one would expect the first resonance for the $J = 2$ partial-wave component to appear somewhat below $D = 0.907 ea_0$, the first for the $J = 3$ component to appear near $D = 0.935$, and so on for higher angular momenta. Sample results for the $J = 2$ partial wave confirmed this conclusion.

IV. COMMENTS AND CONCLUSIONS

From results of the present model study of rotational Feshbach resonances one can reach some general conclusions concerning very-low-energy electron scattering by molecular gases. Rotational resonances associated with real or virtual excitation of the target system from one rotational state to another are obviously possible and for polar molecules are quite probable. The latter point is based on the present observation that such resonances are possible over a reasonable "width" of dipole moments below a critical value and the additional fact that the conditions for which a resonance occurs are a function of the rotational state of the target system. Thus the likelihood of resonances in low-energy molecular scattering is increased by the fact that a large number of rotational states of the target gas are usually populated at room temperature or even lower, and the conditions for a resonance, which may not occur in the ground state, may nevertheless be satisfied in one or more of the other rotational states of the system. We hasten to add that the appearance of rotational resonances for our model system having dipole moments near a critical value does not imply that polar molecules possessing a dipole moment of comparable magnitude would show a similar resonance at the same energy. The dipole contribution in the total electron-polar molecule interaction potential has been shown to given only minimal information on the electron binding property or electron-scattering cross sections for such systems, since other contributions to the interaction potential play a far from negligible role in these processes.[13]

An important question which still remains unanswered is whether similar rotational resonances exist in low-energy electron scattering by simple molecules such as H_2 and N_2.[1] It seems quite reasonable that such phenomena may play a role in explaining the pressure dependence of electron drift velocities in *some* high-pressure drift experiments. The present study clearly indicates that rotational resonances may exist in electron scattering by a molecular field which is insufficient in strength to form either a stable negative ion or an eigenstate of the projected Feshbach Hamiltonian. However, it does not answer whether the nonpolar H_2 and N_2 molecules support similar resonances.[1] One can only infer that the likelihood of such a phenomenon for these molecules is greater for angular momenta which are larger than S wave.

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[15]The contribution to electron binding of a given term in the target eigenstate expansion decreases with increasing angular momentum l. The radial equations behave near the origin as r^{l+1} and become more and more "external" for large l, thus contributing less to the over-all binding.

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